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Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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Shaped refractory articles and process for the manufacture thereof

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Shaped refractory articles and process for the manufacture thereof.

Description.

[0001] The present invention relates to shaped refractory articles comprising ceramic oxides, in particular rollers and to a process for the manufacture of said articles.

[0002] Many ceramic oxides materials are known in the art and widely used. Examples are aluminium based oxides (mullite, alumina, corundum, ...), silicon based oxides (mullite, silica, for example vitreous silica, ...), zirconium based oxides (zirconia, zircon, ...) and the like. In the following description, the invention will be described with reference to vitreous silica. While vitreous silica is indeed the preferred material, it should be clearly understood that, according to the invention, other ceramic oxides can be used.

[0003] Vitreous silica is the generic term to designate the glassy (amorphous or non crystalline) form of silicon dioxide. High purity sand or quartz deposits provide the raw material which is electric arc melted at very high temperature to provide respectively fused silica or fused quartz. Vitreous silica can routinely withstand temperature of over 1250°C, and due to its very low coefficient of thermal expansion can be rapidly heated and cooled with virtually no risk of breakage due to thermal shock. It is tough and hard so that articles made therefrom exhibits good surface damage resistance and superior wear resistance.

[0004] Typically, vitreous silica exhibits a (bulk) density of 1.8 to 2.2 g/cm^3, a coefficient of thermal expansion (at room temperature) of 0.50 to 0.95 10^{-6}/°C, a thermal conductivity of 0.62 to 1.38 W/m.°K and an apparent porosity of 7 to 16 %.

[0005] A number of industrial applications of vitreous silica taking advantage of these properties are known. For example, it can be used as pouring nozzle for the casting of liquid metal for cold start of casting sequences, as rotary degasser for molten aluminium, as crystallisation crucible, as conveyor roller for the transfer of material (such as metal or glass) in the form of sheet, strip or foil in a furnace, etc.

[0006] It has been found that the surface of vitreous silica rolls forming the conveyors used for transferring sheets, strips or foils through a furnace tends to collect deposit of material from the sheets, strips or foils so that sheets, strips or foils passing thereover become scratched and/or dented. The phenomenon of deposit formation is complex and is influenced by the composition of the sheets, strips or foils carried by the rolls and the composition and temperature of the furnace atmosphere as well as the character of the roll surface. Such a deposit is referred to as build-up or pickup and is hereinafter referred to as pickup.

[0007] Such sheets, strips or foils, of course, are not perfect and must be scrapped or given an inferior grade. The simple replacement of these rolls while maintaining the furnace hot is not always possible so that when the rolls reach this stage of pickup, it is often necessary to shut down the furnace until the rolls can be polished by grinders or even replaced. This shutting-down is a long process and a serious curtailment for the production of the furnace. A period of several days may be necessary for cooling down the furnace and further time is required for the

actual polishing or replacement of the rolls before the furnace can again be placed in service. Even in the cases when it is possible to replace the rolls without having to shut down the whole furnace, this requires the uneasy manipulation of hot and heavy articles and raises other problems.

[0008] Several attempts have been made in that art to try to improve the properties of vitreous silica with respect to pickup. So far, the most common approach has been to use a material other than vitreous silica for particularly demanding applications (such as high silicon steel for example). It has thus already been suggested to provide the rolls with special alloy coatings (USP 2,695,248), to use a shaft made from a particular steel grade (USP 4,470,802) or even to use a roller made from a different material such as graphite.

[0009] Some good results have been obtained with relatively "soft" graphite rolls which do not tend to accumulate pickup at their surface. With such rolls, it has been observed that the outer layer of the rolls on which the pickup is formed tends to be eroded by the sheets, strips or foils carried by the rolls faster than the deposit formation so that no pickup can be observed. An obvious disadvantage of such rolls being that due to their weak erosion resistance, they must also often be replaced with all the above discussed problems.

[0010] It is therefore an object of the present invention to provide shaped refractory articles which possess the excellent mechanical properties of vitreous silica articles without showing the pickup problems normally observed with the articles of the art. Such articles should also have a prolonged service life.

[0011] These problems and others have been solved with shaped refractory articles comprising a vitreous silica basis and, homogeneously distributed therein, a carbonaceous material.

[0012] According to a first embodiment, the vitreous silica basis is comprised of a chemically bonded (cement bonded and/or resin bonded) vitreous silica aggregate. Typically, the chemically bonded vitreous silica aggregate is prepared from a mixture comprising (i) at least 75 wt. %, preferably more than 85 wt. %, of amorphous silica, (ii) from 2 to 23 % of a chemical binder and (iii) water. Suitable chemical binders are calcium aluminate, calcium silicate, polyalkoxysiloxanes such as polydiethoxysiloxane (ethylsilicate), colloidal silica, aluminium or zirconium acetate, magnesium oxide, and the like or mixtures thereof. Calcium aluminate is the preferred binder. The mixture is shaped and then dried. It is generally not necessary to fire such a chemically bonded vitreous silica aggregate. The dried chemically bonded vitreous silica aggregate comprises generally from 75 to 96 wt. % of vitreous silica, from 2 to 23 wt. % of the chemically binder and from 2 to 4 wt. % of water.

[0013] According to a second and preferred embodiment, the vitreous silica basis comprises generally at least 60 wt. % of amorphous silica, preferably more than 90 wt. %, more preferably more than 95 wt. % and typically more than 99 wt. %. The vitreous silica forms a matrix and can be obtained by any known process for the preparation of a vitreous silica matrix such as slip casting or injection moulding. The vitreous silica, once shaped is fired. The shape is generally densified by sintering at temperature above 1000°C.

[0014] According to the present invention, refractory shapes comprising a vitreous silica basis are then impregnated with a liquid carbonaceous material such as tar (pitch) or resin. The carbon impregnation reduces the apparent porosity to as low as about 2% or less which, beside reducing the pickup, also serves to further protect the refractory silicon oxide from corrosive attack which otherwise can occur. Pieces to be impregnated are placed into a vessel and air is evacuated. The vacuum is maintained between 15 minutes and 1 hour. This ensures that entrapped air within the internal pores of the article is removed. At this point, liquid resin or tar is introduced into the vessel. The required viscosity of the impregnant is dependent on the pore size of the article. A piece with finely distributed porosity requires low viscosity impregnant to ensure adequate impregnation. The viscosity range is typically between 10-100 centipoise. Higher viscosity resins can be used if thinned with appropriate solvents. Once the impregnant has been introduced to the vessel, a pressure between 5 and 25 bars is typically applied to force the resin or tar into the porosity. This completes the impregnation process.

[0015] Optionally, the article can be heated up to 300°C before or during the impregnation process in order to ensure adequate impregnation.

[0016] An impregnated article is then heated up to 750°C to drive off low temperature volatile compounds. The cured resin or tar can be carbonised to give fixed carbon by heating up to 950°C in a reducing or inert atmosphere.

[0017] Advantageously, the vessel can be highly pressurised (up to 25 bars) to promote the cracking of the cured resin or tar.

[0018] The impregnated article comprises from 1 to 6 wt. % of carbonaceous material. If necessary, the article can be subjected to several impregnation steps to reach the desired amount of carbonaceous material.

[0019] In addition, further refractory materials (oxides, nitrides or carbides) can be incorporated into the ceramic oxide basis. Typically, zircon silicate, aluminium oxide, silicon carbide and silicon nitride or their mixtures will be used. Preferably, they will not represent more than 39 wt. % of the whole article.

[0020] In particular, such an article shaped as a roller exhibits a surprisingly low tendency to pickup while presenting all the above discussed excellent properties of a vitreous silica roller, in particular the resistance to erosion. Consequently, such rollers have a particularly long service life before requiring any grinding or replacement. Conveyor units comprising a plurality of such rolls are advantageously used for the transport of material in the form of sheet, strip or foil in very demanding application such as for the transport of sheet, strip or foil of high silicon steel (oriented grains), stainless steel in an annealing furnace or in a galvanisation line or for the transport of sheet, strip or foil of glass.

[0021] As an example a vitreous silica roller according to the invention has been manufactured and compared with the very same roller but the carbonaceous material. Table I shows various properties measured for the roller (roller 2) according to the invention compared with the same roller before its impregnation with the carbonaceous material (roller 1).

TABLE I

	Roller 1	Roller 2
Absolute (bulk) density (kg/dm^3)	2.208	2.161
Relative density (kg/dm^3)	1.984	2.030
Open porosity	10.14%	6.1%
Average Modulus of rupture (Mpa)	32.674	33.984
Average Pore diameter (μm)	0.11	0.057
Carbon content (wt. %)	0	2.16%

[0022] Rollers 1 and 2 have been installed into a conveyor unit for the transport of high silicon steel strips. The surface of rollers 1 and 2 and of the transported strips was regularly checked during their service life and the results are reported in Table II.

TABLE II

Control time	Roller 1	Roller 2
15 days	A,E	A,E
1 month	B,E	A,E
2 months	B,F	A,E
3 months	C,G	A,E
6 months	C,G	A,E
12 months	D,G	B,E
18 months	___	B,F

Legend: A: no pickup can be observed.
B: some pickup can be observed with a magnifier.
C: some pickup can be visually observed.
D: important pickup. The roller has to be replaced.
E: transported strips are not marked.
F: transported strips are slightly marked.
G: transported strips are so marked that they have to be given a lower grade.

Claims.

1. Shaped refractory article comprising a ceramic oxide basis and, homogeneously distributed therein a carbonaceous material.

2. Shaped refractory article wherein the ceramic oxide basis comprises vitreous silica.

3. Shaped refractory article according to claim 1 or 2, wherein the ceramic oxide basis consists of a chemically bonded ceramic oxide aggregate comprising from 75 to 96 wt. % of ceramic oxide, from 2 to 23 wt. % of a chemically binder and from 2 to 4 wt. % of water.

4. Shaped refractory article according to claim 3, wherein the chemical binder is selected among the group consisting in calcium aluminate, calcium silicate, polyalkoxysiloxanes, colloidal silica, zirconium acetate, magnesium acetate, magnesium oxide and their mixtures and preferably is calcium aluminate.

5. Shaped refractory article according to claim 1 or 2, wherein the ceramic oxide basis consists of a sintered ceramic oxide matrix comprising at least 60 wt. %, preferably more than 90 wt. %, more preferably more than 95 wt. % and even more preferably more than 99 wt. % of ceramic oxides.

6. Shaped refractory article according to claim 5, wherein the article comprises 1 to 6 wt. % of carbonaceous material.

7. Shaped refractory article according to claim 6, wherein the article comprises up to 39 wt. % of a material selected form the group consisting in zircon silicate, aluminium oxide, silicon carbide, silicon nitride and the mixtures thereof.

8. Shaped refractory article according to any one of claims 1 to 7, wherein the article is a roller.

9. Process for the preparation of a shaped refractory article according to any one of claims 1 to 8, **characterized in that** it comprises the steps of
a) preparing a vitreous silica basis,
b) impregnating the vitreous silica basis with a carbonaceous material.

10. Process according to claim 9 wherein the impregnation step is performed under heat.

11. Process according to claim 9 or 10 wherein the impregnation step is performed under pressure.

12. Process according to any one of claims 9 to 11, **characterized in that** the impregnation step is followed by a further step of
c) cracking the impregnated carbonaceous material under heat.

13. Process according to claim 10 wherein the cracking step is performed under pressure.

Abstract of the disclosure.

Shaped refractory articles and process for the manufacture thereof.

The present invention relates to shaped refractory articles comprising a ceramic oxide basis, in particular rollers and to a process for the manufacture of said articles which do not show the pickup problems normally observed with the articles of the art.

The shaped refractory articles of the invention comprise a ceramic oxide basis and, homogeneously distributed therein, a carbonaceous material.